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COMPLETE EQUATION OF STATE FOR β-HMX AND IMPLICATIONS FOR INITIATION

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Abstract. A thermodynamically consistent equation of state for β-HMX, the stable ambient polymorph of HMX, is developed that fits isothermal compression data and the temperature dependence of the specific heat computed from molecular dynamics. The equation of state is used to assess hot-spot conditions that would result from hydrodynamic pore collapse in a shock-to-detonation transition. The hot-spot temperature is determined as a function of shock strength by solving two Riemann problems in sequence: first for the velocity and density of the jet formed when the shock overtakes the pore, and second for the stagnation state when the jet impacts the far side of the pore. For a shock pressure below 5 GPa, the stagnation temperature from the jet is below the melt temperature at ambient pressure and hence insufficient for rapid reaction. Consequently, for weak shocks a dissipation mechanism in addition to shock heating is needed to generate hot spots. When the stagnation temperature is sufficiently high for rapid reaction, the shock emanating from the hot spot is computed, assuming a constant volume burn. For initial shocks below 20 GPa, the temperature behind the second shock is below 1000 K and would not propagate a detonation wave.

INTRODUCTION

Mesoscale simulations, which resolve the explosive grains and hot spots within a plastic-bonded explosive (PBX), are being used to better understand the initiation process. These simulations require as input the constitutive properties of the components of the PBX. A thermodynamically consistent equation of state (EOS) for the stable ambient polymorph β-HMX is developed below based on data from quasi-static compression experiments [1, 2] for the mechanical properties and molecular dynamics calculations of the crystal density of states for the thermal properties [3]. The specific heat is a function of temperature. This is particularly important for simulations that resolve hot spots since the chemical reaction rate is very sensitive to temperature.

The equation of state can be used to scope out hot-spot conditions in order to ascertain the dominant physical processes that a mesoscale simulation of initiation must incorporate. Assuming that hot spots are generated on a fast time scale behind a lead shock,

their rapid heating will result in reaction that can be approximated by a constant-volume burn. The burn results in a high pressure that generates a secondary shock wave emanating from the hot spot. The pressure of the constant-volume burn and temperature of the second shock depend on the strength of the lead shock wave. These quantities are determined by the equation of state.

FREE ENERGY

A thermodynamically consistent equation of state can be defined by the Helmholtz free energy. We assume that the free energy has the form of a generalized Hayes EOS [4]

$$
\begin{aligned}
F(V,T) = & -\int_{V_0}^{V} dV\, P_0(V) \\
& - \theta(V) \int_0^{T/\theta} \frac{d\widetilde{T}}{\widetilde{T}} \left(\frac{T}{\theta(V)} - \widetilde{T} \right) \widehat{C}_V(\widetilde{T}) .
\end{aligned} \quad (1)
$$
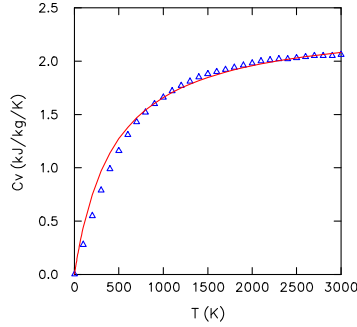
FIGURE 1. Specific heat. Symbols are from molecular dynamics calculations [3, p. 96] and red curve is fit, Eq. (3), used for the EOS model.

A Birch-Murnaghan form is used for the cold curve

$$P_0(V) = \tfrac{3}{2}K_0\left[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}\right]$$
$$\times \left(1 + \tfrac{3}{4}\left[K_0' - 4\right]\left[(V/V_0)^{-2/3} - 1\right]\right). \quad (2)$$

The specific heat is assumed to have the form

$$\widehat{C}_V(\widetilde{T}) = \frac{\widetilde{T}^3}{c_0 + c_1\widetilde{T}^2 + c_2\widetilde{T}^2 + c_3\widetilde{T}^3}, \quad (3)$$

where $\widetilde{T} = T/\theta(V)$ is a scaled temperature. This form has the asymptotically correct limits: $\widehat{C}_V(T) \propto T^3$ for small T and $\widehat{C}_V(T) \to$ const for large T. The Debye temperature is assumed to have the form

$$\theta(V) = \theta_0\left(\frac{V_0}{V}\right)^a \exp\left[b\left(V_0 - V\right)/V\right]. \quad (4)$$

Consequently, the Grüneisen coefficient is given by

$$\Gamma(V) = -\frac{V}{\theta}\frac{d\theta}{dV} = a + b\frac{V}{V_0}. \quad (5)$$

The pressure and internal energy are determined by the standard thermodynamic relations $P = -\partial_V F$ and $e = F - T\partial_T F$.

The EOS parameters for HMX are listed in table 1. These are fit to isothermal compression data [1, 5] and the temperature dependence of the specific heat from molecular dynamic calculations [3, p. 96]. Figures 2 and 3 show a comparison between the data and the model EOS. The discrepancy of the thermal expansion coefficient is due to the neglect of the temperature dependence of either the bulk modulus or Grüneisen coefficient.

TABLE 1. Model EOS parameters for β-HMX.

|		
ρ_0	1.9	g/cm^3
K_0	16.5	GPa
K_0'	8.7	—
a	1.1	—
b	-0.2	—
c_0	$5.2653675003188 \times 10^{-1}$	K·kg/MJ
c_1	$3.0733581008896 \times 10^{2}$	K·kg/MJ
c_2	$1.8318931090834 \times 10^{5}$	K·kg/MJ
c_3	$4.1941409666532 \times 10^{2}$	K·kg/MJ

The sensitivity of the shock temperature to the specific heat is shown in figure 4. For dissipative mechanisms other than shock heating, a constant specific heat can have a large effect on hot spot temperature, and hence on chemical reaction rates.

ESTIMATES FOR INITIATION

One of the proposed mechanisms for generating hot spots is known as hydrodynamic pore collapse [9, §3.3]; the impact of a shock wave on a pore forms a micro-jet which subsequently stagnates on the far side of the pore, converting kinetic energy into thermal energy. This results in a localized region of high temperature, *i.e.*, a hot spot.

The peak hydrodynamic hot-spot temperature can be determined from the EOS as follows. The initial state (density, temperature and velocity) of the jet is determined by solving a Riemann problem between the shocked state of the explosive and the pore (gas or void). Due to convergence the tip of the jet will then accelerate. High resolution hydro simulations [10, these proceedings] show that the velocity of the jet tip can increase by a factor of 2. A second Riemann problem between the jet state and the ambient explosive then determines the hot-spot temperature.

For HMX based plastic-bonded explosives, temperatures over 1000 K are needed for a hot-spot induction time (tens of ns) short compared to the time-to-detonation (hundreds of ns) from Pop-plot data of shock initiation. When this occurs, the fast reaction in the hot spot can be approximated with a constant-volume burn. The pressure rise from the burn then gives rise to a secondary shock emanating from the hot spot. The temperature of the second shock can be calculated from the EOS. The burn states and shock states are shown in figures 5 and 6.
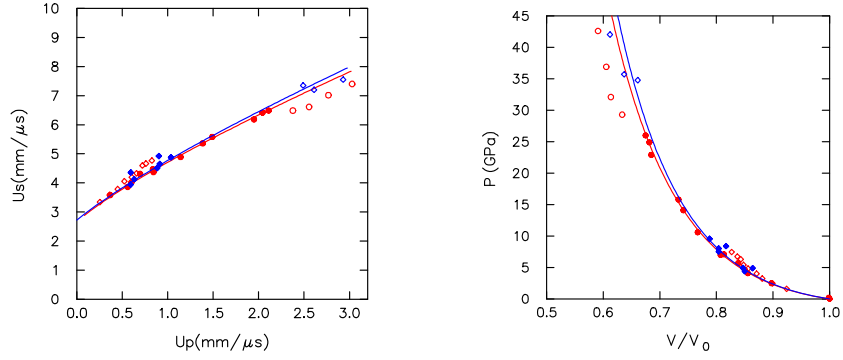
FIGURE 2. Mechanical response of HMX. Red and blue curves are isotherm and Hugoniot loci, respectively, from EOS model. Blue symbols are Hugoniot data [6, pp. 595–596] and red symbols are isothermal data [1, 2]. Open circles are above the pressure induced phase transition reported in [1] and are not used in the calibration of the EOS model.
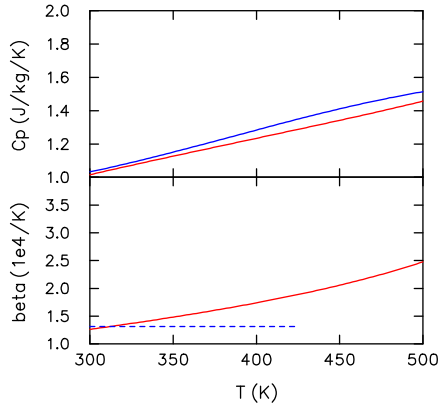
FIGURE 3. Specific heat [7] and the volumetric coefficient of thermal expansion [8] at atmospheric pressure. Blue curve is experimental data and red curve is model EOS.

From figure 6 we see that a hot-spot temperature of at least 1000 K requires an incident shock pressure of about 10 GPa. Moreover, for shocks up to 20 GPa the second shock emanating from fast burning hot-spot has a temperature below 1000 K and is insufficient by itself to initiate a detonation wave. Hence, initiation of a detonation wave must be a collective phenomenon involving many hot spots.

Finally, we note that when the incident shock pressure is below 5 GPa, the hydrodynamic hot-spot temperature is below the melt temperature of HMX, ~ 550 K at ambient pressure. Hence, initiation from weak shocks requires an additional dissipative mechanism to increase the hot-spot temperature.
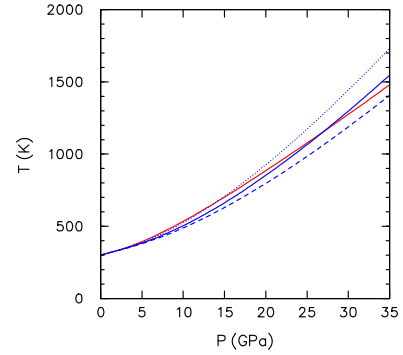
FIGURE 4. Temperature on Hugoniot locus. Red curve is model with temperature dependent specific heat. Blue curves have constant specific heat; $C_V = 1.2, 1.4, 1.6 \times 10^{-3}$ MJ/(kg·K) for dotted, solid and dashed lines, respectively. These values of C_V correspond to $T \simeq 360$ K for dotted curve, temperature near β-δ transition ($T \simeq 440$ K) for solid curve and near the melt temperature at ambient pressure (550 K) for dashed curve.

CONCLUDING REMARKS

To gain an understanding of initiation from hot spots, mesoscale simulations should use chemical reaction rates. For weak shock (pressure below 5 GPa), a dissipative mechanism in addition to shock heating must be included. Proposed mechanisms include frictional heating across closed cracks or grain boundaries, and viscous heating which approximates rate-dependent plasticity. In addition, to evaluate reaction rates reliably, a simulation must accurately compute the temperature. This requires an EOS that
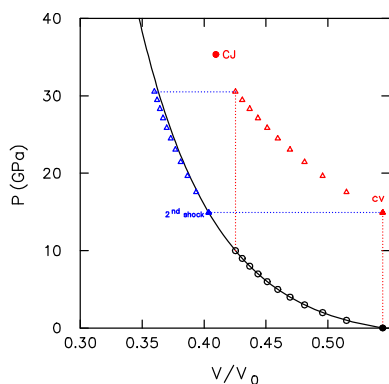
FIGURE 5. Loci relevant to hot spots in HMX. Black line is principal shock Hugoniot. Black circles indicate first shock. Red and blue triangles correspond to constant-volume burn from first shock and second shock to the burn pressure, respectively.

FIGURE 6. Temperature along loci in figure 5 parameterized by the pressure behind the first shock. Black line is temperature on principal shock Hugoniot. Dashed blue line is temperature of second shock at constant volume burn pressure from first shock. Red lines are estimates for hot-spot temperature based on a hydrostatic pore collapse; dashed line assumes no effect from convergence while dotted line assume velocity of jet tip increased by factor of 2.
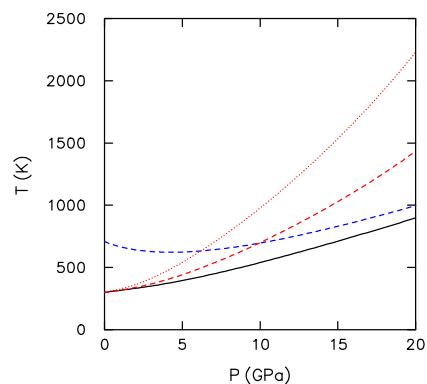
accounts for the temperature dependence of the specific heat.

For HMX the reaction rate is only significant above melting. We note that the latent heat for melting is equivalent to $\Delta T \sim 200\,\mathrm{K}$, and would have a large effect on the reaction rate. Furthermore, when HMX melts the volume change is substantial $\sim 8\%$ and confinement would affect pressure and hence the melt temperature. Constructing an EOS that accounts for melting requires data on the liquid state. Experimentally this would be difficult to obtain because the reaction rate becomes substantial above melting. The best chance for obtaining the needed liquid EOS data is from molecular dynamics simulations.

ACKNOWLEDGMENTS

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